Combining efficiently catalytic hydrodechlorination and wet peroxide oxidation (HDC–CWPO) for the abatement of organochlorinated water pollutants

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Macarena Munoz*, Zahara M. de Pedro, Jose A. Casas, Juan J. Rodriguez

Ingenieria Quimica, Universidad Autonoma de Madrid, Crta. Colmenar km 15, 28049 Madrid, Spain

ABSTRACT

The combination of catalytic hydrodechlorination (HDC) and wet peroxide oxidation (CWPO) has been investigated for the breakdown of chlorophenols (CPs). The process was conducted as a sequential two-step reaction involving 30 min HDC followed by CWPO. Direct application of CWPO to CPs has shown important drawbacks derived from the formation of toxic intermediates under substoichiometric H_2O_2 doses as well as from the fact that the reaction rate decreases significantly as the number of chlorine atoms in the molecule increases (pseudo-first order rate constant values of 20.6×10^{-3}, 4.6×10^{-3} and 1.4×10^{-3} L g_{cat}^{-1} min^{-1} were obtained for 4-CP, 2,4-DCP and 2,4,6-TCP disappearance, respectively). On the opposite, HDC removes chlorine from CPs under mild conditions at a frankly high rate which is almost unaffected by the chlorine content of the starting chlorophenol (values of 0.19, 0.17 and 0.15 L g_{cat}^{-1} min^{-1} for the pseudo-first order rate constants were obtained with 4-CP, 2,4-DCP and 2,4,6-TCP, respectively). Thus, HDC can be used as a short-time pretreatment ($\approx$30 min) associated to a subsequent CWPO step in order to achieve a high mineralization in significantly lower reaction times. The sequential combination of HDC and CWPO as a two-step reaction was tested with different CPs using monometallic catalysts for each step (Pd/γ-Al$_2$O$_3$ and Fe/γ-Al$_2$O$_3$, respectively). This combined process allowed improving TOC reduction from 30% (CWPO alone) to 70% after 120 min reaction time. Moreover, it allowed reaching a substantial reduction of ecotoxicity (>95%) with the three chlorophenols tested.

1. Introduction

The development and implementation of suitable treatments for industrial wastewater containing organochlorinated pollutants has attracted an increasing attention in the last two decades. Fenton oxidation is a well-established process to treat industrial wastewater due to its simplicity as well as its ability to degrade a wide variety of organic pollutants [1–4]. The use of solid catalysts in the so-called catalytic wet peroxide oxidation (CWPO) presents some important advantages respect to the conventional homogeneous Fenton process since the catalyst is not loss in the effluent, thus additionally avoiding the formation of iron sludge upon final neutralization step. Among the catalysts commonly used in CWPO, those based on iron supported on alumina have proved to be highly active and stable in the treatment of different organic pollutants [5–7].

Although CWPO has been widely applied for different persistent organic pollutants, the oxidation of organochlorinated compounds requires special attention. In recent works [8–10] it has been demonstrated that partial oxidation of chlorophenols by Fenton oxidation under substoichiometric H_2O_2 doses leads to the formation of highly toxic condensation species such as chlorinated diphenyl ethers, biphenyls and dibenzofurans. On the other hand, the rate of oxidation of organochlorinated compounds by CWPO decreased significantly as the number of chlorine atoms of the molecule increased due to steric hindrance, which means that polychlorinated pollutants are highly resistant to oxidation [11,12].

Catalytic hydrodechlorination (HDC) appears as a potential emerging technology for the treatment of organochlorinated pollutants since it can be carried out at mild conditions, shows a low sensitivity to pollutants concentration and does not lead to more toxic chlorinated by-products [13,14]. In fact, this technology has been successfully applied with a wide variety of chlorine-containing organic compounds such as chlorophenols, chlorobenzenes, chlorodioxins, chlorodibenzofurans or chlorofluorocarbons [15,16]. Upon HDC organochlorinated compounds react with a source of hydrogen giving rise to HCl and the corresponding de-chlorinated species, which allows reducing substantially the ecotoxicity of the effluent. However, this process does not reduce the amount of total organic carbon (TOC) and thus, the exit stream needs further treatment in order to achieve a high abatement of the organic load.

The combination of HDC and CWPO has been scarcely studied and could represent an effective and environmentally friendly solution for the treatment of aqueous streams containing organochlorinated pollutants [17,18]. HDC can be used as a short-time pretreatment in order to remove the chlorine atoms from the organochlorinated pollutants followed by a CWPO step addressed to TOC reduction. In a recent contribution [18] we developed a bimetallic catalyst, based on Fe and Pd, capable of working efficiently for both HDC and CWPO. However, a significant deactivation was observed upon successive applications, which was attributed to Fe leaching due to the HCl produced upon HDC.

In order to overcome the drawbacks associated to the low stability of the bimetallic Pd–Fe catalyst, in this work the HDC and CWPO steps were carried out with monometallic catalysts of Pd and Fe, respectively, supported on γ-alumina in both cases. Three different chlorophenols were tested as target compounds: 4-chlorophenol (4-CP); 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP). Those chlorophenols have been widely used in the literature as representative of organochlorinated pollutants in industrial wastewater. They constitute a particular group of priority pollutants regarded by the EU [19] and US EPA [20] which can be found in a wide variety of industrial wastewater since they are used in the manufacture of a diversity of chemical products like pesticides, herbicides, germicides, fungicides and wood preservatives. First, an in-depth study of the CWPO of those three CPs was accomplished with an own-prepared Fe/γ-Al$_2$O$_3$ catalyst. A wide range of H$_2$O$_2$ doses was covered in order to identify the by-products formed and follow the evolution of ecotoxicity under different oxidant loads. Secondly, the HDC study was carried out with a Pd/γ-Al$_2$O$_3$ catalyst, also prepared in our lab. The kinetics of the process is analyzed on the basis of the reaction pathway proposed from the identification of by-products. Finally, the effective combination of HDC and CWPO was investigated and the stability of both catalysts (Pd/γ-Al$_2$O$_3$, Fe/γ-Al$_2$O$_3$) was tested in a long-term continuous HDC–CWPO experiment.

2. Materials and methods

2.1. Catalysts preparation and characterization

The catalysts used in this work (Fe/γ-Al$_2$O$_3$; Pd/γ-Al$_2$O$_3$) were prepared by incipient wetness impregnation of powdered γ-Al$_2$O$_3$ supplied by Merck (Germany). Aqueous solutions of Fe(NO$_3$)$_3$·9H$_2$O and PdCl$_2$ were used as precursors for the CWPO (Fe/γ-Al$_2$O$_3$) and HDC (Pd/γ-Al$_2$O$_3$) catalysts, respectively. The Fe and Pd loads were adjusted to 4% and 1% (w/w), respectively. After impregnation, the solids were left for 2 h at room temperature, dried for 12 h at 60 °C and calcined for 4 h at 300 °C [7]. An additional reduction in H$_2$ atmosphere was carried out for 2 h at 350 °C in the case of the Pd/γ-Al$_2$O$_3$ catalyst.

The textural properties of the fresh and used catalysts were characterized from nitrogen adsorption–desorption isotherms at −196 °C using a Micromeritics Tristar 3020 apparatus. The samples were previously outgassed overnight at 150 °C to a residual pressure of <10^{-3} Torr. Total iron and palladium contents were measured by inductively coupled plasma (ICP/MS) with a ICP-MS Elan 6000 Perkin-Elmer Sciex. The carbon content of the used catalysts was determined by a LECO CHNS-932 Elemental Analyzer while the chlorine content was analyzed by total reflection X-ray fluorescence (TRXF), using a TXRF spectrometer 8030c. X-ray photoelectron spectroscopy (XPS) was used for surface analysis with a Thermo Scientific, model k-Alpha equipped with a Kα X-ray excitation source, 1486.68 eV. Software "XPS-Peak" was employed for deconvolution of the XPS profiles. The superficial metal content was calculated from the area of the spectral peaks. Palladium

dispersion on the Pd/γ-Al$_2$O$_3$ catalyst was determined from CO chemisorptions at room temperature in a Micromeritics Chemisorb 2750 automated system equipped with Chemisoft TPx software. Prior to chemisorption measurements, the samples were reduced in H$_2$ flow at 350 °C for 2 h. A 1:1 stoichiometry was taken for CO adsorption over the Pd atoms [21,22].

Characterization of the porous structure of the raw alumina and the synthesized Fe/γ-Al$_2$O$_3$ and Pd/γ-Al$_2$O$_3$ catalysts confirmed their mesoporous character since the BET and the external or non-microporous areas were almost coincident. Impregnation of the support did not practically affect the BET surface area (138 m^2 g^{-1} for γ-Al$_2$O$_3$ vs. 136 and 134 for the Fe/γ-Al$_2$O$_3$ and Pd/γ-Al$_2$O$_3$ catalysts, respectively). According to the ICP-MS analyses the Fe and Pd content of the fresh catalysts were close to the nominal 4% and 1% (w/w) (3.9% and 0.95%, respectively). The content of chlorine of the fresh catalyst (0.37) was determined by TXRF. This value is similar to those found in other Pd catalysts prepared from palladium chloride and no significant effect on the activity of the catalysts was detected in previous works [23–25].

The XPS analyses of the Pd/γ-Al$_2$O$_3$ catalyst served to establish the relative concentration of zero valent (Pd^0) and electrodeficient (Pd^{n+}) palladium species. According to previous works [26–28] both species are required for HDC of organochlorinated compounds. The Pd^{n+}/Pd^0 ratio of the fresh catalyst obtained by XPS was around 0.7. On the other hand, the CO chemisorption measurements revealed a fairly high dispersion of the active phase (33%) with a mean particle diameter of 3.5 nm. The ratio of the superficial (XPS) to the total (ICP) Pd content of the catalyst was 0.69, which indicates a quite homogeneous distribution of the active phase onto the alumina particles.

2.2. Experimental procedure

Both, the HDC and CWPO experiments were conducted in a 500 mL jacketed glass batch reactor stirred at 700 rpm to avoid mass-transfer limitations. A catalyst concentration of 2 g L^{-1} was always used, in powdered form (dp <100 μm). The HDC runs were carried out at 30 °C and H$_2$ was continuously passed at 50 N mL min^{-1}. The use of H$_2$ gas excess would not represent a drawback for HDC since the exit gas stream can be easily recycled to the reactor [29]. Mono-, di- and trichlorophenols were used as target pollutants at 200 mg L^{-1} initial concentration for 4-CP and 2,4-DCP and 100 mg L^{-1} for 2,4,6-TCP which can be considered representative in different industrial wastewater [30–32]. Those chlorophenols were also selected in order to study the effect of the chlorine content on the degradation rate upon CWPO and HDC. The Cl/Pd molar ratios corresponded to 8.4, 13.2 and 8.1 for 4-CP, 2,4-DCP and 2,4,6-TCP, respectively. The CWPO experiments were carried out at 50 °C, which according to the literature allows achieving a high efficiency of H$_2$O$_2$ consumption [3,33,34]. The initial pH value of the reaction medium was adjusted to 3 with nitric acid and the H$_2$O$_2$ dose corresponded always to the theoretical stoichiometric amount for complete mineralization. A previous set of CWPO experiments were performed at high initial concentrations of chlorophenols (2000 mg L^{-1}) in order to better identify the reaction by-products. In this case, different H$_2$O$_2$ doses were used, covering from 20% to 100% of the theoretical stoichiometric amount for complete conversion of CPs into CO$_2$, H$_2$O and HCl.

The combination of HDC and CWPO was carried out as a sequential two-step reaction involving 30 min HDC followed by CWPO. The stability of the catalysts was tested in a HDC–CWPO sequential treatment in long-term continuous experiments using two stirred tank reactors in series. The effluent from the HDC stage was directly fed to the second tank where CWPO was accomplished.

Three replicates of each experiment were carried out. The data reproducibility was better than ±5% in all the cases. Preliminary

blank experiments were conducted which confirmed the very low adsorption of chlorophenols by the Fe/γ-Al$_2$O$_3$ or Pd/γ-Al$_2$O$_3$ catalysts prepared in this work (less than 5% reduction of the initial concentration).

2.3. Analytical methods

The progress of the HDC and CWPO processes was followed by periodically withdrawing and analyzing liquid samples from the reactors. The catalysts were separated by filtration with a PTF filter (0.45 μm). The analytical methods and equipments used in this work have been described in detail elsewhere [18].

The aromatic and condensation chlorinated by-products formed upon CWPO of chlorophenols were analyzed by extracting samples in n-hexane at the end of each run. The extracted samples were analyzed by gas chromatography with mass spectrometry detection (GC/MS) with an electron impact ionization source (Saturn 2100T). The capillary column used was a Factor Four, Varian (30 m length, 0.25 mm internal diameter). To confirm the structural assignment of the identified compounds, analytical standards were used, as well as the NIST 05 library.

2.4. Ecotoxicity tests

Toxicity testing has grown steadily in recent years and is a useful tool in environmental risk assessment. It refers to the potential of chemical stressors to affect living organisms. Since assays based on animals, plants and algae are expensive, time consuming and require large sample volume, recent studies have emphasized the benefits of rapid, reproducible and cost-effective bacterial assays for toxicity screening and assessment. *Vibrio fischeri* inhibition assay is recognized in the literature as the most sensitive test, economic, easy to operate and requiring only 5–30 min for toxicity prediction [35]. In this sense, the ecotoxicity of the starting chlorophenol and the reaction samples was determined by the Microtox® toxicity test using *V. fischeri* (ISO 11348-3, 1998). The bioluminescence was measured in a M500 Microtox Analysis (Azur Environmental). The test was conducted at 15 °C, adjusting the osmotic pressure close to 2% NaCl and the pH between 6 and 8. The EC$_{50}$ is used to quantifiy the ecotoxicity of a compound. It is defined as the effective nominal concentration (mg L^{-1}) that reduces the intensity of light emission by 50% after 15 min contact time. For complex samples IC$_{50}$ is used, defined as the reciprocal of the dilution percentage giving rise to 50% light emission reduction. The EC$_{50}$ and IC$_{50}$ values are inversely proportional to the ecotoxicity expressed as toxicity units (TU).

3. Results and discussion

3.1. Chlorophenols breakdown by CWPO

Consistently with previous works [7,36] the reactivity of CPs decreased as the chlorine content of the molecule increased (pseudo-first order rate constant values of 20.6×10^{-3} L g$_{cat}$$^{-1}$ min^{-1}, 4.6×10^{-3} L g$_{cat}$$^{-1}$ min^{-1} and 1.4×10^{-3} L g$_{cat}$$^{-1}$ min^{-1} were obtained for 4-CP, 2,4-DCP and 2,4,6-TCP disappearance, respectively). The dechlorination percentage ([Cl$^-$]$_i$/[Cl]$_0$) also showed the same trend, achieving values of 82%, 58% and 27% for 4-CP, 2,4-DCP and 2,4,6-TCP upon 120 min reaction time. This fact seems to be closely related to steric hindrance since less sites are available in the aromatic ring for hydroxyl radical attack. On the other hand, Cl and OH are *ortho* and *para* directors in the aromatic ring, which explains that Fenton oxidation of 3-CP is faster than that of 4-CP, which is oxidized more easily than 2-CP [37]. However, those authors also concluded that as the number of chlorine atoms increases from 1 to 3, steric

Table 1
Chlorophenol and TOC conversion upon CWPO of the three CPs tested at different H$_2$O$_2$ doses ([4-CP]$_0$ = [2,4-DCP]$_0$ = 2000 mg L^{-1}; [2,4,6-TCP]$_0$ = 100 mg L^{-1}; [H$_2$O$_2$]$_0$ = stoichiometric dose; pH$_0$ = 3; T = 50 °C). The values are taken after complete H$_2$O$_2$ conversion ($t_R \leq$ 24 h).

Chlorophenol	20%		50%		75%		100%	
	X_{CP}	X_{TOC}	X_{CP}	X_{TOC}	X_{CP}	X_{TOC}	X_{CP}	X_{TOC}
4-CP	89.2	18.5	99.7	48.7	100	65.6	100	74.4
2,4-DCP	86.1	19.4	98.4	49.1	100	71.9	100	77.8
2,4,6-TCP	75.3	19.2	94.2	48.3	100	74.3	100	88.9

hindrance becomes more and more important in determining the oxidation rates and the *ortho* and *para* director effect of Cl seems to play a less and less important role.

The results obtained upon CWPO of CPs at different H$_2$O$_2$ doses are summarized in Table 1. As observed, complete conversion of chlorophenol required in all cases H$_2$O$_2$ doses above 50% of the stoichiometric. At this H$_2$O$_2$ dose the percentage of mineralization is somewhat lower than 50%. Increasing that dose up to the stoichiometric led to a significant improvement of mineralization, more accused as the chlorine content of the starting CP increased. Almost 90% mineralization was achieved for 2,4,6-TCP although that required 24 h reaction time.

The results obtained in this work considerably improve those previously reported in the literature in terms of mineralization, namely TOC reduction, upon CWPO of chlorophenols. Moreover, those works have been commonly carried out using H$_2$O$_2$ doses above the stoichiometric amount. Molina et al. [38] studied the oxidation of 4-CP using Al–Fe pillared clays as catalysts. These authors reported TOC reductions from 31% to 42% using the stoichiometric dose of H$_2$O$_2$ and two times this amount, respectively, under the following operating conditions: 100 mg L^{-1} 4-CP, 1 g L^{-1} catalyst, pH 3 and 25 °C. Catrinescu et al. (2011) [39] also evaluated the oxidation of 4-CP (125 mg L^{-1}) with Al–Fe pillars (1 g L^{-1}) prepared from different host clays (two reference "source" clays (SA$_Z$-1 and SW$_Y$-2) and montmorillonite (M$_t$)). The experiments were performed with the stoichiometric dose of H$_2$O$_2$ at 50 °C and pH 3.5. TOC reductions of 60, 50 and 45% were achieved with Mt, SA$_Z$-1 and SW$_Y$-2 catalysts, respectively. More recently, Xu and Wang [40] carried out the oxidation of 4-CP with Fe$_3$O$_4$/CeO$_2$ composites, reaching 66% TOC removal. The experiments were carried out with 2 g L^{-1} catalyst and three times the stoichiometric amount of H$_2$O$_2$ at 30 °C and pH 3.

3.1.1. Condensation by-products

According to the results so far CWPO appears an interesting solution for chlorophenols-bearing wastewater. In fact, some other works in the literature support that conclusion also on the basis of high CPs conversion and TOC reduction [41,42]. However, some additional issues need to be considered as well, being the reaction by-products and the evolution of ecotoxicity among the most important. As a representative example, Table 2 shows the effect of the H$_2$O$_2$ dose on the distribution of by-products obtained upon CWPO of 2,4-DCP (see Tables S1 and S2 of Supplementary material for 4-CP and 2,4,6-TCP results). Chlorobenzenediol (4-chlorocatechol) was detected as a main reaction intermediate, resulting from hydroxylation of the aromatic ring in the *ortho*- position. Different dichlorobenzenediols (2,4-dichloro-1,5-benzenediol and 2,4-dichloro-1,6-benzenediol) were also detected in trace amounts at the lowest dose of H$_2$O$_2$ tested. As it is well-known, ring-opening of aromatic intermediates led to the formation of short-chain organic acids. Their concentration increased with the H$_2$O$_2$ dose up to 75% of the stoichiometric and beyond that decreased upon mineralization. The reaction pathways proposed on the basis of the results obtained for the three chlorophenols

Table 2
Reaction by-products (milligrams of carbon per liter) upon CWPO of 2,4-DCP with the Fe/γ-Al$_2$O$_3$ catalyst at different H$_2$O$_2$ doses (Rest of conditions as in Table1).

Compound	H$_2$O$_2$ (% of the stoichiometric dose)			
	20	50	75	100
Residual 2,4-DCP	123.1	14.4	0.0	0.0
4-Chlorocatechol	23.1	0.0	0.0	0.0
Condensation by-products	497.1	152.3	2.6	0.0
Maleic acid	6.5	15.5	6.4	0.4
Fumaric acid	5.2	17.8	0.0	0.0
Malonic acid	3.3	99.1	52.9	31.3
Acetic acid	6.1	7.9	6.6	11.6
Chloroacetic acid	3.2	12.6	13.2	9.9
Oxalic acid	5.4	76.1	92.8	51.2
Formic acid	9.5	33.3	49.6	24.6
Chlorine balance closure (%)	66	88	98	99

tested have been included in the Supplementary Material (Figs. S1–S3).

The differences between the measured TOC values and the calculated from the identified by-products (chlorobenzenediols and short-chain organic acids) together with the unconverted chlorophenols were attributed to the formation of condensation by-products. Significant amounts of those compounds were obtained under subsotoichiometric H$_2$O$_2$ doses whereas they were completely degraded working at the stoichiometric H$_2$O$_2$ dose (Table 2). It is expected that the condensation by-products contain chlorine since, as shown in Table 2, the chlorine balance only matched almost completely at H$_2$O$_2$ doses above 50% of the stoichiometric. The formation of high amounts of condensation by-products is supported by the development of a brownish color in the reaction medium at substoichiometric H$_2$O$_2$ doses (see Fig. S4 in the Supplementary material). The reaction medium undergoes a dramatic change of color as H$_2$O$_2$ decreased below the stoichiometric evolving from colorless to dark brown. H$_2$O$_2$ doses above 75% of the stoichiometric produced colorless effluents. These results are consistent with the obtained upon conventional Fenton oxidation [10]. However, in that case significant amounts of chlorinated diphenyl ethers, biphenyls and dibenzofurans were found, whereas in CWPO only a chlorinated diphenyl ether was detected (*m*/*z* 290) whose concentration was around 5 mg L^{-1} at 20% of the stoichiometric H$_2$O$_2$ dose, not appearing at higher H$_2$O$_2$ doses. These results suggest that important amounts of condensation by-products could be adsorbed onto the catalyst. The color of the Fe/γ-Al$_2$O$_3$ catalysts after the oxidation experiments support this hypothesis showing a dark brown color at fairly substoichiometric H$_2$O$_2$ doses (20% and 50% of the stoichiometric amount) (see Fig. S4 in the Supplementary material). For a more conclusive information, Table 3 summarizes the elemental composition as well as the BET surface area of the catalyst after being used in the CWPO of 2,4-DCP (see Table S3 in Supplementary material for 4-CP and 2,4,6-TCP). The C, H and Cl contents of the used catalyst increased considerably when the H$_2$O$_2$ dose decreased below the stoichiometric amount.

Table 3
Chemical and textural characterization of the Fe$_2$O$_3$/γ-Al$_2$O$_3$ catalyst before and after being used in the CWPO of 2,4DCP at different H$_2$O$_2$ doses.

Catalyst sample	H$_2$O$_2$ dose (% stoich.)	Composition (%)			BET surface area (m^2 g^{-1})
		C	H	Cl	
Fresh catalyst	–	0.06	0.57	0.00	138
Used catalyst	20	7.71	0.99	2.74	92
	50	5.04	0.72	1.63	103
	75	3.14	0.69	0.49	111
	100	2.15	0.67	0.31	124

Table 4
Evolution of ecotoxicity (TU) upon CWPO (4 h) of chlorophenols at 50 °C under different initial H$_2$O$_2$ doses. ([2-CP]$_0$ = [4-CP]$_0$ = [2,4-DCP]$_0$ = 2000 mg L^{-1}; [2,6-DCP]$_0$ = 900 mg L^{-1}; [2,4,6-TCP]$_0$ = 100 mg L^{-1}).

Chlorophenol	Initial sample	H$_2$O$_2$ dose (% of the stoichiometric)			
		20	50	75	100
2-CP	102.4	222.7	6.3	2.4	0.3
4-CP	1052.6	204.2	5.4	1.8	0.2
2,4-DCP	408.2	265.1	4.0	3.9	0.7
2,6-DCP	75.5	78.1	4.1	3.2	0.4
2,4,6-TCP	7.9	4.4	0.3	0.1	0.0

Simultaneously, the BET area of the catalyst decreased, thus confirming the existence of deposits on its surface.

The characteristics of this residue appear similar to the polymeric species resulting from homogeneous Fenton oxidation of CPs [8–10]. It was soluble in 0.1 M NaOH (see Fig. S5 in Supplementary material), which is a common feature of humic acid-like species. This type of compounds typically consists in a complex mixture containing carboxyl and phenolate groups, able to form complexes with iron.

3.1.2. Ecotoxicity study

The ecotoxicity values of the effluents from CWPO after 4 h of reaction at 50 °C under a wide range of H$_2$O$_2$ doses were measured and compared with those of the initial chlorophenols solutions. The results are summarized in Table 4. As can be observed, the resulting effluents showed similar or even higher ecotoxicity values than the starting chlorophenols solutions when a dose of 20% of the stoichiometric amount of H$_2$O$_2$ was used, which is directly related to the presence of chlorinated condensation by-products. Dramatic reductions of ecotoxicity were achieved increasing the H$_2$O$_2$ dose up to 50% of the stoichiometric which proves the potential detoxifying ability of CWPO for industrial wastewaters containing chlorophenols although the crucial importance of adjusting the H$_2$O$_2$ must be considered as well as assuming high reaction times in the case of polychlorinated compounds.

The ecotoxicity of the starting chlorophenol solutions are in good agreement with those previously reported in the literature [14,43]. The ecotoxicity values of the effluents from CWPO are also consistent with previous works [44–46]. For instance, Perez-Moya et al. [45] demonstrated that partial degradation of 2-chlorophenol by Fenton oxidation led to highly toxic effluents. In the same way, Shang et al. [44] reported an increase of ecotoxicity upon incomplete ozonation of monochlorophenols. Similar conclusions were reported by Andreozzi et al. [46] upon photocatalytic oxidation of 3,4-dichlorophenol.

3.2. Catalytic hydrodechlorination

So far it is proved that the oxidation rate is highly dependent on the number of chlorine atoms of the chlorophenol and that at low H$_2$O$_2$ doses highly toxic chlorinated by-products are formed. Since H$_2$O$_2$ consumption represents a critical issue on the ecotoxicity of CWPO and Fenton-like processes in general, we have analyzed the convenience of using hydrodechlorination as a pretreatment step, using an own-prepared Pd/γ-Al$_2$O$_3$ catalyst. Although some differences were observed in the HDC rate between mono-, di- and trichlorophenols (values of 0.19 L g$_{cat}^{-1}$ min^{-1}, 0.17 L g$_{cat}^{-1}$ min^{-1} and 0.15 L g$_{cat}^{-1}$ min^{-1} were obtained for the pseudo first-order rate constant of 4-CP, 2,4-DCP and 2,4,6-TCP disappearance, respectively), all of them were completely degraded at 30 min reaction time, which reduces significantly the reaction time required to remove those compounds upon CWPO. The HDC of polychlorinated phenols led to the formation of
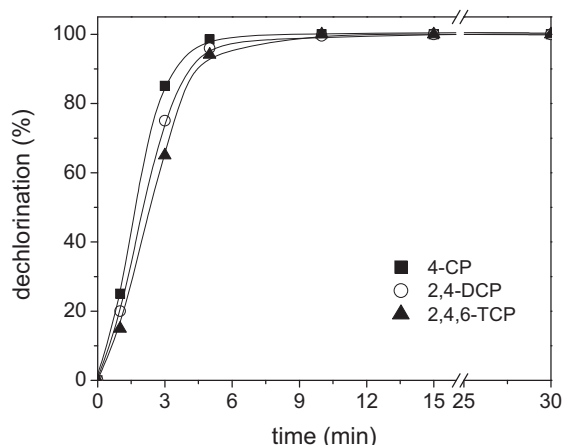
Fig. 1. Evolution of the dechlorination percentage upon HDC of 4-CP, 2,4-DCP and 2,4,6-TCP with the Pd/γ-Al$_2$O$_3$ catalyst (2 g L^{-1}). ([4-CP]$_0$ = [2,4-DCP]$_0$ = 200 mg L^{-1}; [2,4,6-TCP]$_0$ = 100 mg L^{-1}).

intermediate chlorophenols. Thus, 2,4-dichlorophenol gave rise to 2-chlorophenol and 4-chlorophenol, whereas 2,4,6-TCP led to 2,4-DCP and 2,6-DCP. However, it has to be highlighted that complete dechlorination was achieved after 30 min (Fig. 1), being all the chlorine present in the reaction medium in form of chloride ion. At that time, the selectivity to phenol was higher than 95% in all cases being cyclohexanone the only other reaction by-product (Table 5). The closure of carbon and chlorine balances based on the identified species was always above 95%.

The products obtained upon HDC of chlorophenols in this work are in good agreement with those previously reported in the literature [14,25,28,47] where phenol has commonly been obtained as the main reaction product. Further hydrodechlorination of chlorophenols with Pd-bearing catalysts gives rise to the formation of increasing amounts of cyclohexanone [18,29]. However, the aim of the HDC treatment in this work is only achieving the complete dechlorination of the molecule in order to improve the oxidation rate of the effluent upon CWPO. It is also worthy of mentioning that the HDC pretreatment allowed a significant reduction of the ecotoxicity of the effluents (more than 50% of reduction in all cases in 30 min reaction time).

3.3. CPs degradation by HDC–CWPO sequential treatment

The combination of catalytic hydrodechlorination and oxidation for the treatment of organochlorinated pollutants has been scarcely studied so far. Yalfani et al. [17] studied the degradation of chlorophenols by that combination using formic acid and oxygen as reactants at ambient conditions (25 °C). They achieved up to 70% and 80% for TOC and ecotoxicity reduction, respectively. In a recent contribution [18] the oxidation of synthetic mixtures of phenol and cyclohexanone, the two aforementioned by-products from HDC of chlorophenols, was studied. It was demonstrated that a high phenol

Table 5
Dechlorination percentage, products selectivity and ecotoxicity values of the effluents obtained upon HDC (30 min) of 4-CP, 2,4-DCP and 2,4,6-TCP with the Pd/γ-Al$_2$O$_3$ catalyst (2 g L^{-1}). ([4-CP]$_0$ = [2,4-DCP]$_0$ = 200 mg L^{-1}; [2,4,6-TCP]$_0$ = 100 mg L^{-1}).

Chlorophenol	Dechlorination	S_{Ph}	S_{C-one}	Ecotoxicity (TU)	
	(%)			Initial CP solution	HDC effluent
4-CP	100	95.9	4.1	105.3	11.3
2,4-DCP	100	96.3	3.7	40.8	9.1
2,4,6-TCP	100	94.1	5.9	7.9	3.8
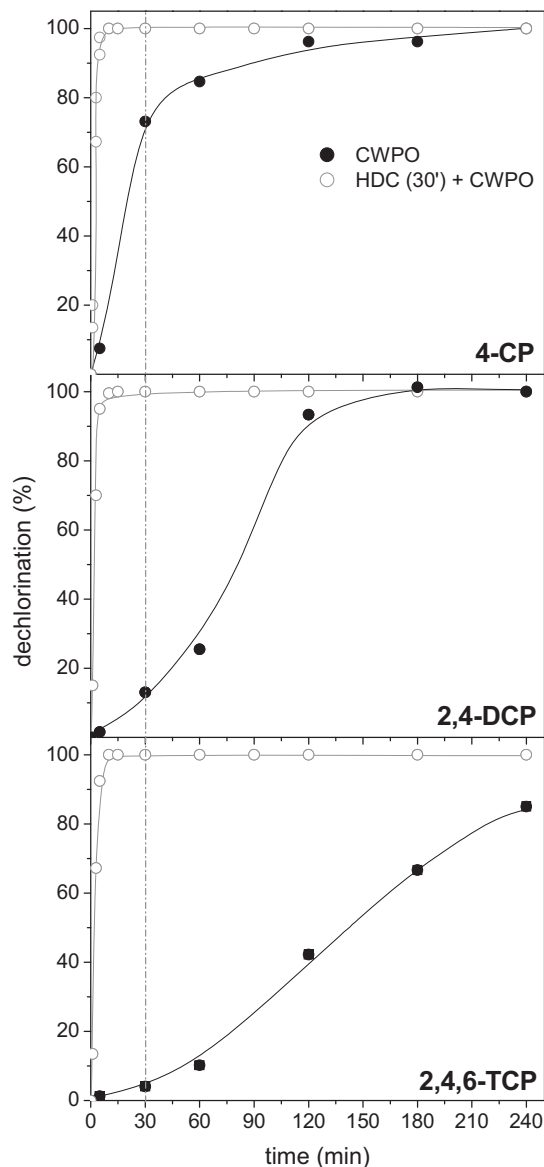
Fig. 2. Evolution of the dechlorination percentage upon CWPO and HDC + CWPO of chlorophenols (H$_2$O$_2$ at the stoichiometric dose; catalysts at 2 g L^{-1}).

concentration promotes the oxidation of all the organic species, but the presence of cyclohexanone hinders the formation of aromatic radicals, thus limiting the efficiency of the CWPO step. Therefore, the effective combination of HDC and CWPO requires that the HDC step achieves the complete dechlorination of chlorophenols but restricting as much as possible further hydrogenation. In this sense, a combination of a short HDC pretreatment (30 min) followed by a CWPO step was tested in the current work.

The combination of HDC and CWPO represents a significant advantage with respect to CWPO alone, not only because it avoids the formation of highly toxic chlorinated by-products, but also due to the considerable increase of the kinetics of dechlorination and mineralization, as can be seen in Figs. 2 and 3. The differences between CWPO alone and the combined sequential HDC + CWPO treatment were more pronounced as the chlorine content of the target chlorophenol increased. This fact can be clearly appreciated with 2,4,6-TCP, achieving its complete dechlorination upon the 30 min HDC step while 4 h were required for its disappearance upon CWPO alone. Meanwhile, the rate of mineralization was significantly improved, as it is clearly appreciated in Fig. 3 where
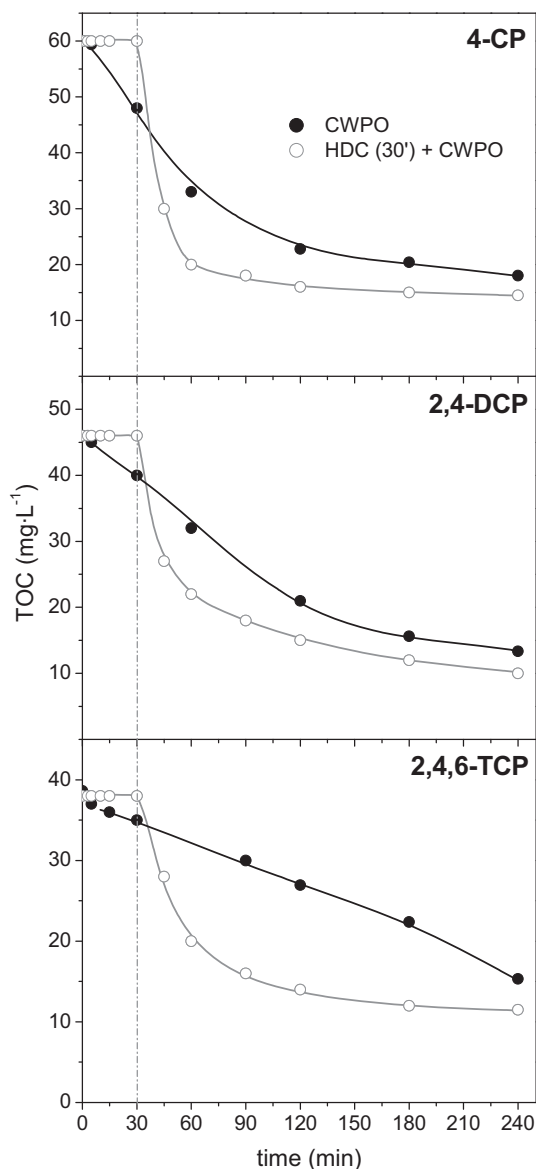
Fig. 3. Evolution of TOC upon CWPO and HDC + CWPO of chlorophenols (H$_2$O$_2$ at the stoichiometric dose; catalysts at 2 g L^{-1}).

at 120 min 70% mineralization of 2,4,6-TCP was achieved with the HDC + CWPO treatment whereas only 30% was reached with CWPO alone. It has to be highlighted that the final products obtained upon HDC + CWPO of CPs were short-chain organic acids (malonic, acetic, oxalic and fomic) without significance in terms of ecotoxicity.

3.3.1. Stability of the catalysts

The stability of the catalysts was tested in a HDC–CWPO sequential treatment in long-term continuous experiments using two stirred tank reactors in series and 2,4-DCP as target compound. The results are depicted in Fig. 4. As can be seen, both the HDC (Pd/γ-Al$_2$O$_3$) and the CWPO (Fe/γ-Al$_2$O$_3$) catalysts showed a highly stable performance.

The high stability of the Pd/γ-Al$_2$O$_3$ catalyst in HDC of chlorophenols has been previously reported in the literature [48,49]. This fact is related to the strong metal support interactions, which makes it resistant to catalyst deactivation [50]. In fact, Pd leaching was negligible upon the 100 h on stream. Meanwhile, the leaching of iron from the CWPO catalyst over that time on stream
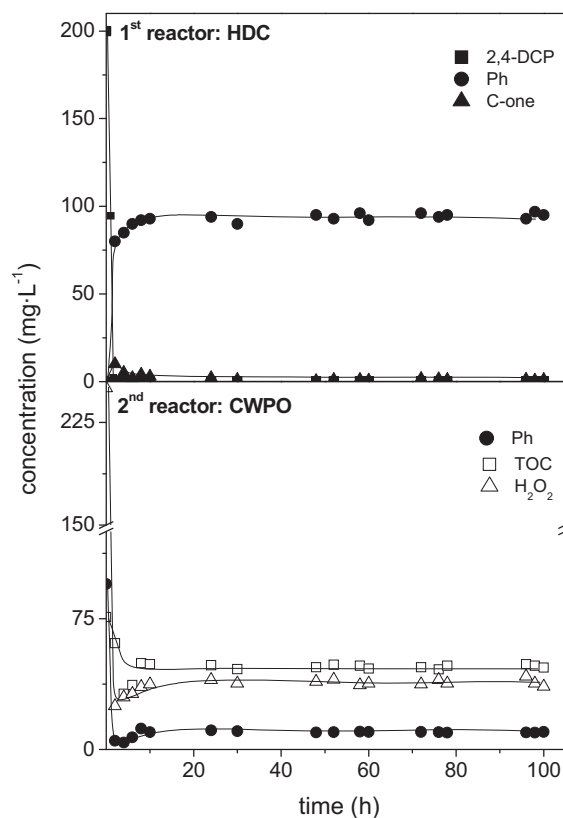

Fig. 4. Results of a long-term continuous experiment for the treatment of 2,4-DCP by the combination of HDC and CWPO ([2,4-DCP]$_0$ = 200 mg L^{-1}; [Pd/γ-Al$_2$O$_3$]$_0$ = 1 g L^{-1}; [Fe$_2$O$_3$/γ-Al$_2$O$_3$]$_0$ = 1 g L^{-1}; [H$_2$O$_2$]$_0$ = 50% of the stoichiometric dose).

was lower than 3% of the initial load. The remarkable stability of this catalyst is also in agreement with the results obtained in previous works dealing with CWPO of phenol and chlorophenols [6,7].

4. Conclusions

Although CWPO is an effective technology for the treatment of chlorophenols, it can lead to the formation of highly toxic by-products, which can be adsorbed onto the surface of the catalyst and also remain in solution. It has also been demonstrated that the oxidation rate of CWPO is highly affected by the chlorine content of the starting chlorophenol. On the opposite, HDC avoids the formation of condensation by-products, thus reducing progressively the ecotoxicity of the effluent. Moreover, the rate of HDC is not strongly affected by the number of chlorine substituents of the chlorophenol molecule, allowing complete dechlorination upon 30 min reaction time at 30 °C. In this sense, the combination of HDC followed by CWPO represents an effective solution for the abatement of chlorophenols in water, allowing complete dechlorination together with a high mineralization in a significantly shorter time than CWPO alone. The resulting effluents showed very low values of ecotoxicity.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.12.029.

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